

## DISPERSED PHASE MOLYBDENUM CATALYST RECOVERY IN COPROCESSING

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### INTRODUCTION

Dispersed-phase molybdenum catalysts are being used at PETC to enhance the simultaneous conversion of petroleum bottoms material and coal to distillate products. A series of tests were performed in micro-autoclaves, 1-liter semi-batch stirred autoclaves, and a 1-liter continuous unit aimed at maximizing the production of distillates while minimizing the catalyst requirements [1]. Similar product yield structures and conversions have been demonstrated using molybdenum concentrations from 200 ppm (based on coal weight) to 1000 ppm in the 1-liter continuous unit. Dispersed-phase catalysis using molybdenum may require catalyst recovery. This paper examines the potential for the recovery of a dispersed-phase molybdenum catalyst.

Molybdenum catalyst recovery schemes typically involve ashing the non-distillate process residue and converting the metals to their oxide form. Certain metal oxides are selectively solubilized by dissolution in ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), including molybdenum, which forms water-soluble ammonium heptamolybdate. A recovery process patented by AMAX [2] involves mixing a gasifier residue with an alkali metal hydroxide, heating the mixture between 600°C and 800°C in the presence of air, adding water to the mixture, and then acidifying and ammoniating the aqueous solution to extract and selectively crystallize as ammonium heptamolybdate. Universal Oil Product Incorporated [3,4] (UOP) has recovered a dispersed vanadium catalyst by first performing a particle size classification of the reactor product with hydroclones, followed by calcination (ashing) of the solids at 500°C, and extraction with an ammonium hydroxide solution.

Earlier experiments at PETC [5] indicated that the nickel and vanadium, present as contaminants in the petroleum bottoms, appear to be incorporated into the carbonaceous material. Thus, these metals are also present in the bottoms material produced in dispersed-phase catalytic coprocessing along with the catalyst and coal mineral matter. The catalyst recovery procedure consisted of extracting the reactor product with tetrahydrofuran (THF), ashing the extract at elevated temperature, and extracting the ash with an ammonium hydroxide solution. Initial recovery experiments used the ASTM procedure for ashing coal [6]. The effects of ashing temperature, coal mineral matter, and the choice of hydroxides (strength of the base) on molybdenum recovery were examined.

### EXPERIMENTAL

Reagents were ACS grade and obtained from Alfa Chemicals. Coals used included an Illinois No. 6 (Burning Star Mine) hvBb coal that was ground to less than 75 microns, and a deep-cleaned Kentucky (Blue Gem Mine) hvAb coal that was ground to less than 7.5 microns and physically cleaned by the Otisca T-Process [7]. Analyses of the feed coals and the coal ash are presented in Table 1. Maya atmospheric tower bottoms (Maya ATB) was used as the vehicle. An analysis of the Maya ATB is

presented in Table 2.

The semi-batch 1-liter autoclave was charged with 150 grams of coal, 350 grams of oil, and 35 grams of 0.045 M ammonium molybdate solution. The unit was operated with a continuous gas stream ( $3\frac{1}{2}\text{H}_2\text{S}:97\frac{1}{2}\text{H}_2$ ) at a rate of 4 SCFH (113 standard liters/hr). Water and volatile products (light oils) from the reactor were condensed in a trap maintained at room temperature. The reactor was maintained at run temperature for 2 hours, cooled, depressurized, drained, and washed with methylene chloride to quantitatively recover the product. Typical heatup and cool-down times of the autoclave tests were two hours. All semi-batch experiments were performed using reactor conditions of 435°C, 2500 psig, and 2 hours residence time.

The catalyst recovery scheme is depicted in Figure 1. Reactor product was slurried with a 5:1 wt ratio of n-heptane and then decanted. The heptane insoluble residue was then washed/extracted with THF and pressure-filtered through a 0.45 micron Durapore® membrane filter, using a 142-mm Millipore Hazardous Waste Filtration System and 40 psig nitrogen. The THF-insoluble residue was vacuum dried and weighed. A portion of the insoluble residue was ashed in a Fisher Model 495 Programmable Ashing Furnace. The residue was heated at a rate of 5°C/min to 250°C, held for an hour at 250°C, heated to the final temperature (700°C, 675°C, 510°C), and held at temperature for 600 minutes.

Solubilizations of the ash were performed at 65°C for one hour. Five grams of ash were used for experiments conducted with residues produced from Illinois No. 6 coal. One or three grams of ash were used for experiments that were conducted with residues produced from Kentucky (Blue Gem) coal or coal-free experiments. The ash was first mixed with approximately 100 ml of deionized water. Ammonium hydroxide was then added to give a weight ratio of ammonia-to-molybdenum of 10:1 and the mixture diluted to 300 ml with additional deionized water. A magnetic stirrer provided agitation during the solubilization. A water-cooled condenser prevented some vapors from escaping. The suspension was then filtered hot in a 47-mm Millipore vacuum filtration apparatus using a water aspirator. The ammonium hydroxide-soluble filtrate was evaporated to dryness using a rotoevaporator. Both the soluble and insoluble filter cakes were dried in a vacuum oven.

Selected samples were examined by thermogravimetric analysis (TGA), scanning electron microscopy (SEM) energy dispersive analysis, X-ray diffraction, and inductively couple plasma emission spectroscopy (ICP). TGA was performed in a Perkin-Elmer TGS-2 Thermogravimetric system using a temperature profile of 5°C per minute in an air atmosphere. Samples were examined with an SEM equipped with an energy-dispersive spectrometer. ICP analysis was carried out at the University of Pittsburgh Applied Research Center (UPARC) using a Bausch and Lomb ARL Model S34000 system.

## RESULTS AND DISCUSSION

By ashing at 700°C and extraction with ammonium hydroxide, over 95 % of the molybdenum could be recovered from physical mixtures of coal ash, molybdenum trioxide, vanadium pentoxide, and nickel oxide. When experiments were performed using residues generated from continuous unit operations, only 50 percent of the molybdenum could be recovered in the ammonium hydroxide soluble extract. Since the melting point of  $\text{V}_2\text{O}_5$  is 695°C, the ashing temperature was reduced to 675°C. Recoveries

of molybdenum were still unsatisfactory. Consequently, a series of semi-batch experiments were performed using different feedstocks and dispersed molybdenum catalyst to produce samples that could determine the effects of ashing temperature, other metals present, and of coal ash constituents on catalyst recovery.

The first set of experiments, experiment A in Table 3, were performed with a THF-insoluble reactor product from liquefaction reactions conducted with Maya ATB and catalyst. The THF-insoluble residue was ashed at a temperature of 675°C producing a glassy solid. The glassy solid was difficult to remove from the crucible and extract with  $\text{NH}_4\text{OH}$ . SEM analysis indicated that the glassy solid was chemically homogeneous to a resolution of 1 cubic micron. X-ray diffraction analysis of the ash was unable to identify the major constituent of the ash.  $\text{MoO}_3$ ,  $\text{NaVMoO}_6$ , and  $\text{Fe}_4\text{V}_2\text{Mo}_2\text{O}_{20}$  were identified as minor constituents. The literature suggested [8] that vanadium-molybdenum complexes form at temperatures of 635°C and that lowering the ashing temperature to below 635°C would eliminate the formation of this complex and possibly the glassy solid.

The effect of ashing temperature on carbon removal from a THF-extracted reactor product was studied by TGA. The weight profile versus temperature indicated that carbon loss was occurring at temperatures as low as 510°C. By lowering the ashing temperature to 510°C, the ash obtained was the expected consistency and weight. Experiments were repeated at the lower ashing temperature of 510°C, (experiment B in Table 3), and the ash produced was a granular material rather than a glassy solid. X-ray diffraction analysis of the ash identified  $\alpha\text{-MoO}_3$  and  $\text{NaVMoO}_6$  as the major constituents of the ash. The unidentified major constituent observed at the higher ashing temperature (675°C) was not present. In an attempt to identify the compound present in the 675°C ash, a sample was ashed at 600°C. The 600°C ash sample contained the unidentified compound,  $\text{NaVMoO}_6$ ,  $\text{Na}_2\text{V}_2\text{Mo}_2\text{O}_{15}$ , and  $\beta\text{-MoO}_3$  as major constituents. Thus the molybdenum bound with the vanadium at 510°C is transformed to more complex structures at 600°C and possibly even more complex structures at 675°C which are inhibiting the recovery of molybdenum. Extraction of the 510°C ash residue with  $\text{NH}_4\text{OH}$  resulted in solubilization of the molybdenum and recoveries were greater than 90 percent. In these experiments, and all subsequent experiments, recoveries are defined as the percentage of molybdenum that is recovered in the basic solution. The range of values in Table 3 for molybdenum purity and ammonium molybdate recovery were from multiple experiments. Solubilized fractions were not selectively crystallized to recover the pure heptamolybdate salt.

The second set of experiments, experiments C and D in Table 3, were done to determine the effect that coal ash has on molybdenum recovery. Semi-batch liquefaction experiments were performed with Illinois No. 6 coal, Maya ATB, and catalyst. The THF-insolubles were ashed at a temperature of 510°C and extracted with  $\text{NH}_4\text{OH}$  but the recovery of molybdenum as a soluble species was only approximately 50 percent. X-ray diffraction analysis of the ammonium hydroxide-insoluble material indicated the presence of calcium molybdate. ICP analysis indicated a 1:1 molar ratio of calcium to molybdenum, consistent with the identification of calcium molybdate by X-ray diffraction.

Experiments were performed to determine if the formation of  $\text{CaMoO}_4$  was interfering with molybdenum recovery. Semi-batch experiments, experiment E in Table 3, were performed using a deep cleaned coal, Kentucky Blue Gem, containing 0.8 wt% ash, rather than the Illinois No.

6 coal containing 11.1 wt% ash. The purpose of using a deep-cleaned bituminous coal was to reduce the effect of the calcium (present in the coal mineral matter) on molybdenum recovery. The THF-insoluble residue was ashed and extracted with  $\text{NH}_4\text{OH}$  and the observed molybdenum recovery as a soluble species was now greater than 95 percent. The results of these experiments demonstrate that the calcium present in the mineral matter reacts with  $\text{MoO}_3$  in the ashing step to form  $\text{CaMoO}_4$ .  $\text{NH}_3$  does not appear to be a strong enough base to react with  $\text{CaMoO}_4$  to solubilize molybdenum.

Pure calcium molybdate was treated with  $\text{NH}_4\text{OH}$  at temperatures as high as  $90^\circ\text{C}$  but it was unreactive and not solubilized. Since ammonium hydroxide was ineffective, the stronger base, sodium hydroxide, was tested. Calcium molybdate was decomposed to form insoluble calcium hydroxide and soluble sodium heptamolybdate when treated with sodium hydroxide. These results demonstrate that stronger bases, such as sodium hydroxide, are capable of decomposing calcium molybdate and removing calcium as an insoluble salt. It also suggests that sodium hydroxide might be used as a substitute for ammonium hydroxide. Treatment of a solution containing sodium heptamolybdate with  $\text{NH}_4\text{OH}$  should result in the selective crystallization of ammonium heptamolybdate, the catalyst precursor.

A typical material balance for metals in a run made with cleaned Kentucky Blue Gem coal is indicated in Figure 2. Molybdenum present as ammonium heptamolybdate comprises 78 percent of the  $\text{NH}_4\text{OH}$ -soluble material. Analyses were not performed for the remaining constituents of the soluble fraction. Experiments with Illinois No. 6 coal typically did not yield as high an ammonium heptamolybdate concentration in the  $\text{NH}_4\text{OH}$ -soluble material. It is thought that some of the coal ash components are being solubilized with the ammonium hydroxide. Typically, for these experiments, molybdenum accounts for 50 percent of the  $\text{NH}_4\text{OH}$ -soluble material.

#### CONCLUSIONS

It has been demonstrated that molybdenum can be recovered from coal liquefaction coprocessing experiments. High recoveries of molybdenum required an ashing temperature of  $510^\circ\text{C}$  to avoid the formation of a refractory molybdenum-vanadium complex, which appeared to form at higher ashing temperatures ( $675^\circ\text{C}$ ) and inhibited molybdenum recovery. X-ray diffraction and elemental analyses of the ash produced from experiments that used coal indicate the presence of calcium molybdate in the ammonium hydroxide-insoluble material. Calcium molybdate that is formed from calcium in the coal mineral matter and the molybdenum catalyst is unreactive with ammonium hydroxide and inhibits the recovery of molybdenum. This was supported by conducting experiments with deep-cleaned coal wherein most mineral matter, to include calcium, had been removed. More than 90% of the molybdenum was recovered from deep-cleaned coal. Preliminary experiments have shown that stronger hydroxides, such as sodium hydroxide, react with calcium molybdate to form a soluble molybdate salt and would result in improved molybdenum recovery. As a result of optimizing the conditions, a recovery scheme has been developed that can recover the molybdenum when calcium has been removed from the feed coal. This scheme most likely will apply to raw coals using sodium hydroxide as a substitute for ammonium hydroxide.

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#### DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Analysis of Feed coals.

	Illinois No. 6 Burning star	Cleaned Kentucky Blue Gem Mine
Ultimate Analysis, wt% (Moisture Free)		
Carbon	70.2	80.3
Hydrogen	4.8	5.1
Nitrogen	0.9	1.9
Sulfur	3.1	0.8
Oxygen(difference)	9.9	11.1
Ash	11.1	0.8
Major Elements in Ash		
SiO <sub>2</sub>	44.6	29.1
Al <sub>2</sub> O <sub>3</sub>	18.3	25.9
Fe <sub>2</sub> O <sub>3</sub>	21.9	25.1
TiO <sub>2</sub>	0.9	3.2
P <sub>2</sub> O <sub>5</sub>	0.1	0.4
CaO	5.1	4.9
MgO	0.6	1.4
Na <sub>2</sub> O	1.6	1.4
K <sub>2</sub> O	1.1	1.7

Table 2. Analysis of Vehicle oil.

	Maya ATB 650°F <sup>+</sup>
Ultimate Analysis, wt%	
Carbon	84.5
Hydrogen	10.6
Nitrogen	0.5
Sulfur	4.0
Oxygen(direct)	0.3
Ash	0.1
850°F (Vol%)	30
Heptane insols, wt%	20
Nickel (ppm)	70
Vanadium (ppm)	370

Table 3. Effect of extraction conditions on Molybdenum recovery.

Exp	Coal	Solvent	Ni+V gm	Mo gm	Ash temp °C	Ash gm	Recovery Mo in sols wt%	(NH <sub>4</sub> ) <sub>2</sub> Mo <sub>7</sub> O <sub>24</sub> Purity wt% sols
A	None	Maya	0.23	1.6	675	4.0	ND	ND
B	None	Maya	0.23	1.6	510	4.2	88	73
C	Ill # 6	Maya	0.15	2.4	675	20.0	35	44
D	Ill # 6	Maya	0.15	1.0	510	18.5	49 - 57	34 - 38
E	Blue Gem	Maya	0.15	1.0	510	3.4	90 - 98	66 - 78

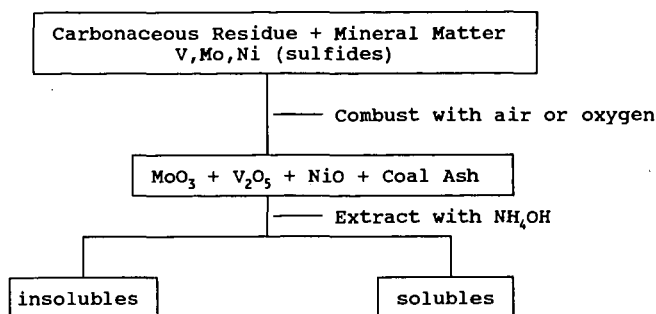


Figure 1. Catalyst Recovery in Coprocessing.

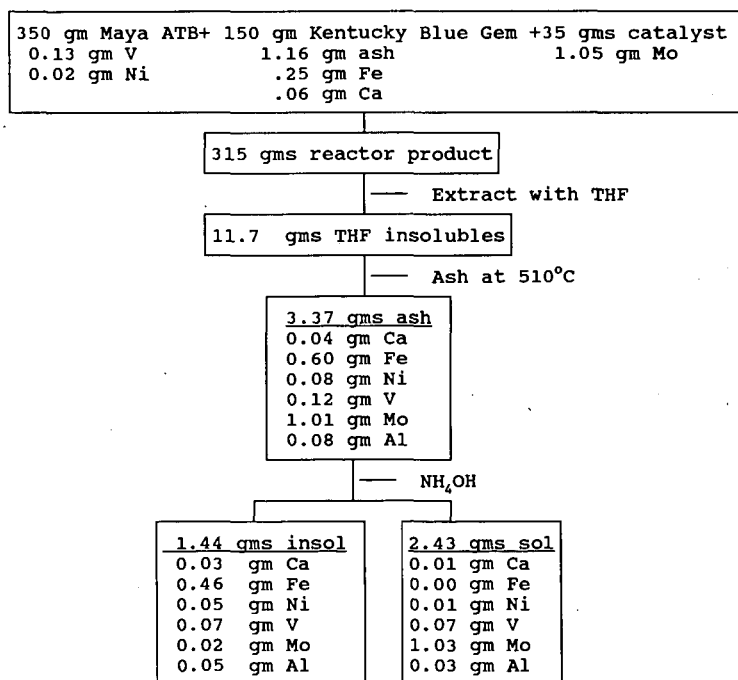


Figure 2. Catalyst Material Balance for Batch Run